APPENDIX I

NOTICE OF INTENT

IMPERIAL
COUNTY NO. 13

№ 1843 PERMIT NO. 13-93-130265[illegible]

NOTICE OF INTENT TO APPLY RESTRICTED MATERIALS ☐ And/Or RECOMMENDATION ☐

COMP. DATE

GROWER—PERMITTEE: Alex Abatti Jr Farming

NOTIFIED

LAST TREATED: 15 Mar 93

LOCATION: Dogwood 24 North | RANCH | SEC 21 | TWN 15 | RNG 14 | MAP ID 7

HAR. DATE EST.

ACRES: 70 | COMMODITY/SITE: Alfalfa | DILUTION/VOLUME GALS | RATE PER ACRE: 5 GALS

APPLICATION DATE: 30 March 93 | AIR - FW - REL - G

SUPPLIER: Rockwood & Helena | INVOICE # | NOTIFIED | W.O. #

PEST CONTROL OPERATOR: Alex Abatti Jr Farming | ADDRESS | NOTIFIED

RATE/AC	PTS QTS / GALS - LBS	PESTICIDE	TOTAL
1.25	(PTS) QTS / GALS - LBS	Furadan 4F (Rockwood)	11 GAL
.5	PTS - QTS / GALS - LBS	Dizzinon AG500 (Helena)	5 GAL
	PTS - QTS / GALS - LBS	(Rockwood) 10-12-0	1 GAL
	PTS - QTS / GALS - LBS		
	PTS - QTS / GALS - LBS		

PESTS:

Pest	
ALF CATERPILLAR	
ALF WEEVIL	✓
APHIDS	✓
ARMYWORM	
BEETLES	
BOLLWORM	
BUDWORM	
CHALCID FLY	
CRICKETS	
CUTWORM	
GRASSHOPPERS	
LEAF MINER	
LEAF PERFORATOR	
LEAFHOPPER	
LOOPER	
LYGUS BUG	
PINK BOLLWORM	
SALT MARSH CATERPILLER	
SPIDER MITES	
SPOTTED ALF APHID	
STINK BUG	
THRIPS	
WHITEFLY	
WEEDS	
DEFOLIATION / DES	
MILDEW	

ENVIRONMENTAL CHANGES: No Bloom in field. No geese widgeon or Coots are known to be frequenting the treatment area for feeding

Surrounding area: Alfa | Alfa | House
Alfa | N / W TREAT AREA E / S | Alfa
Alfa | Sugar beet | Wheat

RESTRICTIONS:
48 HRS./DAYS RE-ENTRY
____ AFTER DRIFT & VAPOR GONE
____ AFTER SPRAY DRIES
14 DAYS TO HARVEST
____ DAYS TO PASTURE
____ DO NOT FEED OR GRAZE LIVESTOCK ON CROP WASTE FOR ____ DAYS
✓ AVOID DRIFT TO SURROUNDING AREAS
✓ TOXIC TO BIRDS, BEES, FISH & WILDLIFE

REMARKS — SPECIAL INSTRUCTIONS — C-WR-B-HB-NIS-ED-WIN-PAS-I-W-O-W-GRI-CR-EQ-SD-CUL-LB-N..

EVALUATION CRITERIA

☐ Sweep Counts ☑ % Infestation ☑ Alternate mitigation measures have been considered
☐ Trap Counts ☐ Preventative ☑ Economic Damage Imminent

SUBMITTED AND/OR RECOMMENDED BY: [signature] | LICENSE NO. 6637 | FILE DATE 29 Mar 93 | TIME

AGRICULTURAL COMMISSIONER: [signature] 3/29/93 | DATE | APPROVED / DENIED

APPENDIX II

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Carbofuran Monitoring in Imperial County during Spring, 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C93-013A

Date: May 19, 1993

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

Protocol for Carbofuran Monitoring
In Imperial County during Spring, 1993

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) Engineering Evaluation Branch (EEB) will conduct a 3-day source impacted ambient monitoring program upwind and downwind of an application of carbofuran to determine concentrations near an application. Carbofuran is a broad spectrum insecticide used on a wide variety of crops for various pests. A report on the measured concentrations will be submitted to DPR.

II. Sampling

A stainless steel valve down stream of the sampling medium will be used to control all sample flow rates. The flow rate will be set and checked with a calibrated flowmeter. Carbofuran will be collected on a bed of XAD-4 resin. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

Prior to application, background samples will be taken to establish if any carbofuran is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with DC-powered pumps capable of flows of approximately 16 liters per minute. Sample collection will follow the timetable outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" as closely as is reasonably possible.

Five samplers will be used; each approximately 20 yards from the perimeter of the field. Four will be placed at the center of each face (assuming a rectangular field) of the field. The fifth sampler will be collocated with one of the other samplers to obtain precision data. These distances and locations are approximate and dependent on the physical obstacles surrounding the field. ARB's "Quality Assurance Plan for Pesticide Monitoring" will be followed as closely as possible.

III. Analysis

All samples will be analyzed by the Department of Environmental Toxicology (DET), University of California, Davis. The resin will first be extracted with ethyl acetate to remove carbofuran. The carbofuran will be separated on a DB-5 (or similar) column and measured with a thermionic specific detector (nitrogen/phosphorous).

IV. Quality Assurance

Field sampling and laboratory analytical quality assurance activities are described in the ARB's "Quality Assurance Plan for Pesticide Monitoring."

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data, including field size, application rate, formulation, and length of the application.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

APPENDIX III

QUALITY ASSURANCE PLAN

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Geneviève Shiroma, Chief
Toxic Air Contaminant
Identification Branch

_____, Chief
Quality Management and Operations
Support Branch

_____, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
	A. QUALITY ASSURANCE POLICY STATEMENT	1
	B. QUALITY ASSURANCE OBJECTIVES	1
II.	SITING	1
III.	SAMPLING	2
	A. BACKGROUND SAMPLES	2
	B. SCHEDULE	2
	C. BLANKS AND SPIKES	2
	D. METEOROLOGICAL DATA	2
	E. COLLOCATION	3
	F. CALIBRATION	3
	G. FLOW AUDIT	3
	H. LOG SHEETS	3
	I. PREVENTATIVE MAINTENANCE	3
	J. TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY	4
	K. TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE	5
IV.	PROTOCOL	6
V.	ANALYSIS	6
	A. STANDARD OPERATING PROCEDURE	6
VI.	FINAL REPORTS AND DATA REDUCTION	8
	A. AMBIENT REPORTS	8
	B. APPLICATION REPORTS	8
	C. QUALITY ASSURANCE	9

APPENDIX

I.	CHAIN OF CUSTODY FORM	10
II.	APPLICATION CHECKLIST	11

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, **ambient** and **application** are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: ___/___/___
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: _____

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX IV

LABORATORY REPORT

Pilot Monitoring Study of Two Pesticides in Air

Contract # 92-314

Date: December 1993

Takayuki Shibamoto
Chuck Mourer
Gregory Hall

Department of Environmental Toxicology
University of California, Davis

The statements and conclusions in this report are those of the University and not necessarily those of the State Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Table of Contents

(1) Literature Search 3

(2) Preliminary Gas Chromatography 3

(3) Air Trapping Efficiencies 3
Table I, Carbofuran Trapping Efficiency Study 5

(4) Method Validation 6
Table II, Carbofuran Method Validation Study 6

(5) Freezer Stability Studies 6
Table III, Carbofuran Freezer Recovery Study 7

(6) XAD-4 Resin Preparation 7

(7) Gas Chromatography 9

(8) Method Validation 9
Table IV, Method validation Samples 9

(9) Submitted Air Samples 10
Table V, Submitted Air Samples 11

(10) Submitted Quality Assurance Samples 12
Table VI, Submitted Quality Assurance Samples 12

Analysis of the Insecticide, Carbofuran, in Air

The Department of Pesticide Regulation (DPR) has requested that the California Air Resources Board (ARB), as part of their toxic air contaminants program, determine airborne exposure to selected pesticides. Candidate pesticides for exposure analysis included carbofuran.

(1) Literature Search

A computer-aided literature search for air sampling and analytical methodology was done on the pesticide. The 950 references generated by the computer search of Chemical Abstracts were assessed for any applicable methodology. Files maintained in the laboratory were reviewed for pertinent methodological information. Notebooks on previous projects referenced by pesticide in the Trace Analytical Laboratory (TAL) were assessed. Files maintained by the Environmental Toxicology Documentation Center by pesticide were evaluated for relevant articles.

(2) Preliminary Gas Chromatography

The trapping efficiency, initial validation and freezer storage samples were analyzed using a Hewlett-Packard Model 5890 series II gas chromatograph equipped with a nitrogen-phosphorous detector and a Model 7673 autoinjector. The column was a "Megabore" 30 m x 0.53 mm ID DB-5. Flows for helium carrier, nitrogen makeup, air and hydrogen were, respectively, 10, 20, 120, 3 ml/min. The injector and detector temperatures were 280°C. The oven temperature program was 180°C initial with no hold, programmed to 240°C at 20°C/minute with a final hold of four minutes.

(3) Air Trapping Efficiencies

A high volume Staplex air sampler was run for 24 hours. The

air sampler had a manifold with four pairs of sampling cups (see Figure I). Sampling cups were comprised of a 4.0 cm x 12.1 cm Teflon cartridge with caps, a 100 mesh stainless steel retainer screen, 30 ml of pre-cleaned (see resin preparation) XAD-4 macroreticular resin, a glass wool plug and a top cap. The sampling cups were assembled by: (1) pressing the 100 mesh stainless steel screen into one end of the cartridge as a retainer for the sampling medium, (2) attaching an end cap, (3) pouring the resin in at the other (inlet) end on top of the screen, (4) inserting a glass wool plug, and (5) attaching the inlet cartridge cap. Two sampling cartridges were connected together with Teflon tubing, inlet to outlet and a funnel securely attached to the top sampling cup inlet. The assembled sampling cup pair was then attached to the manifold tubing of the air pump by the outlet of the bottom sampling cup. Spiking was done by slowly adding 100 μl of 1.00 mg/ml solutions (in acetone) onto the funnel using a Hamilton syringe. Three sampling cup pairs on the air sampler were spiked with 100 μg each of carbofuran, and the fourth pair was an unspiked control. The air pump was started and the measured air flows at the funnel ranged from 48 to 67 liters/min (data not shown). After 24 hours of running, the sampling cups were disassembled. The funnels were washed repeatedly with ethyl acetate into a volumetric flask using a disposable pipette until a total of 50 ml was reached. The resin was poured into a 125 ml erlenmeyer flask, the corresponding glass wool added, the flask sealed and the sample extracted on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The results for the carbofuran in Table I indicated good trapping efficiency (>90%) with no measurable breakthrough to the back resin, and good recoveries (>90%).

Figure I

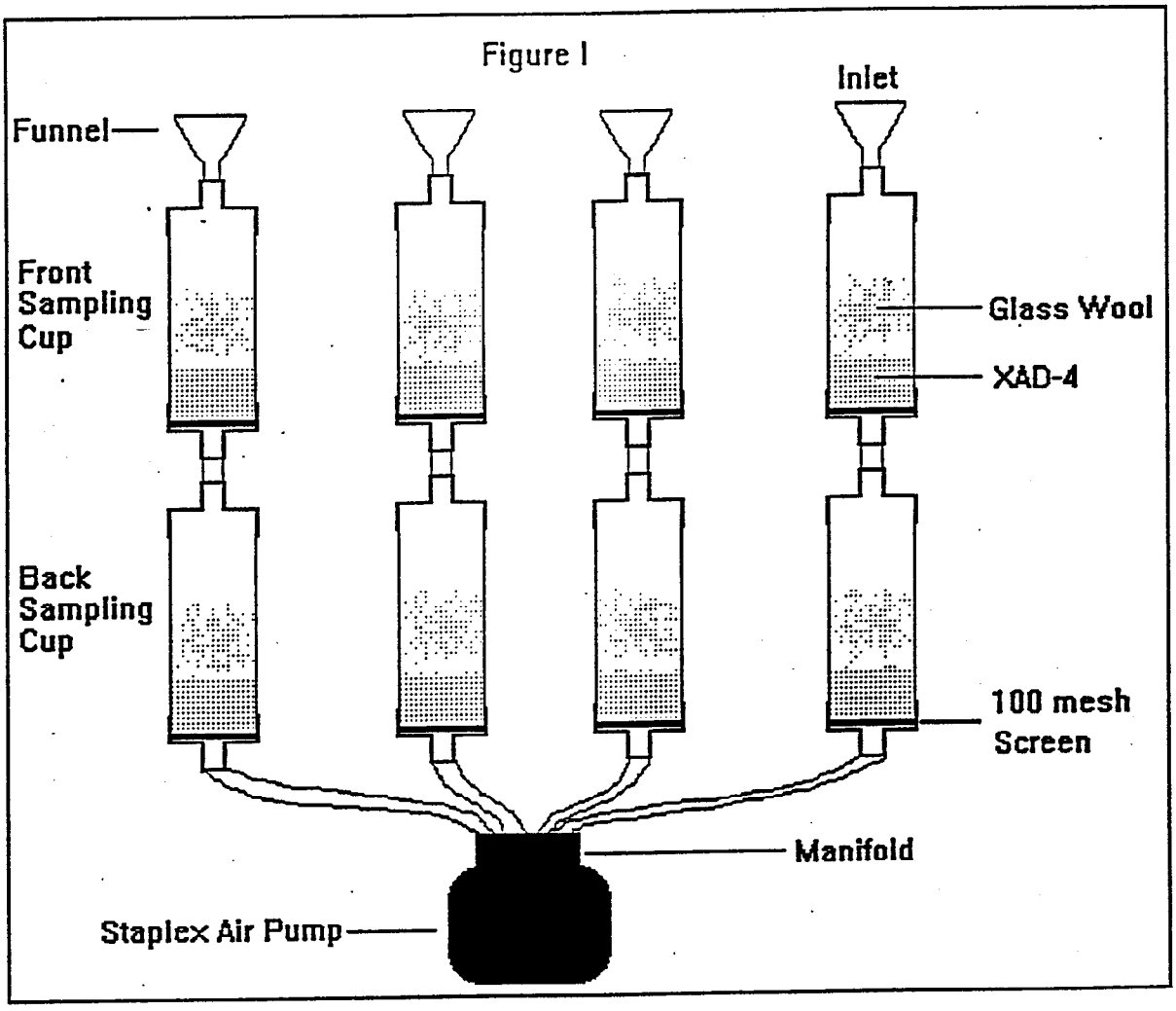

Table I, Carbofuran Trapping Efficiency Study, 100 µg Spike

	% Recovery			
Sample	Funnel	Front Resin	Back Resin	Total
Rep 1	60.9	36.0	<1	96.9%
Rep 2	45.3	50.4	<1	95.7%
Rep 3	56.0	38.4	<1	94.4%
Average =	54.1	41.6	<1	95.7%
SEM* =	5.6	5.5		0.9%
Control	<1	<1	<1	<3

Carbofuran% trapping efficiency = [41.6 x 100]/[100-54.1] = 90.6%

*Note: SEM = Standard Error of the Mean = square root((variance/(n-1))

(4) Method Validation

Seven 125 ml erlenmeyer flasks were prepared by adding 30 ml of XAD-4 resin to each flask. One hundred microliters of carbofuran (1.00 mg/ml in ethyl acetate) was added to the resin in a pair of flasks using a 100 µl Hamilton syringe. Similarly, 100 µl of 0.1 mg/ml was added to second pair of flasks, and 100 µl of 0.01 mg/ml was added to a third pair. The seventh flask was used as a control. The solvent was allowed to evaporate, and 80 ml of ethyl acetate was added to each flask. The flasks were sealed and then placed on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results shown in Tables II had good extraction recoveries (>95%) from the resin.

Table II, Carbofuran Method Validation Study*

Amount Spiked (µg)	Replicate 1	Replicate 2	Ave % Recovery	SEM
100	104.9	112.0	107.9	2.2
10	102.6	94.8	98.7	2.4
1	99.7	98.7	99.2	2.2
			101.5	1.6

*Note: <1% of carbofuran found in control samples at all spiked levels.

(5) Freezer Stability Studies

Nineteen wide mouth screw-top glass jars, 5 cm diameter x 8.5 cm high were prepared by adding 30 ml of XAD-4 resin to each jar. One-hundred microliters each of carbofuran (1.00 mg/ml in ethyl acetate) was added to the resin in jars 1, 2 and 3 using a 100 µl Hamilton syringe. Similarly, 100 µl of 0.1 mg/ml was added to 4, 5, 6, and 100 µl each of

0.01 mg/ml were added to 7, 8 and 9. One jar was used as a control. The solvent was allowed to evaporate, the jars capped and placed in a freezer at -20°C for twelve days. The jars were removed and allowed to come to room temperature. Eighty mililiters of ethyl acetate was added to each jar, capped and extracted on a rotating platform for a minimum of 30 min. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results in Tables III reflect no degradation of the compound over the twelve day interval and complete extraction from the resin, (>95%) in all cases.

Table III, Carbofuran Freezer Recovery Study*

Amount Spiked (μg)	Replicate 1	2	3	Ave % Recovery	SEM
100	90.6	92.2	92.2	91.7	0.6
10	110.0	110.7	110.0	110.1	0.4
1	108.7	111.3	101.2	107.0	3.7
				102.9	3.2

*Note: <1% of carbofuran found in control samples at all spiked levels.

(6) XAD-4 Resin Preparation

1. A 61 x 29 cm cylindrical Pyrex container (approx. 40 l) was thoroughly cleaned with soap and water.
2. Sixteen liters of XAD-4 resin (see note) was added to the container.
3. One gallon of methanol (Resi-grade or equivalent) was added. The resin will expand in the presence of organic solvents. This prevented rapid expansion of the resin.
4. The container was filled with deionized (DI) water with the hose placed at the bottom of the container and stirred vigorously.

5. A vacuum apparatus was prepared with a stiff tube covered at the inlet end with gauze and the outlet end connected to a large trap.
6. As the resin settles, the "fines" were vacuumed-up. When the gauze became covered with "fines", they were wiped off and discarded.
7. The container was re-filled with DI water and stirred.
8. Steps #6 and 7 were repeated until the water above the resin was clear.
9. The pH of the water was checked (usually about 10 from the bicarbonate coating of the resin).
10. Two liters of 0.25 N hydrochloric acid were added and stirred for 30 minutes.
11. The pH of the water was checked and then as much water as possible was removed with vacuum.
12. If the pH was >5 (the pH of our DI water), then new water was added and steps 9 to 11 repeated (usually at least 10 times).
13. Add 1 gallon of methanol and let stand overnight.
14. Pour slurry back into empty solvent bottles.
15. Eight pairs of "knee high" nylons were extracted in the thimble of a Soxlet extractor using ethyl acetate as the extraction solvent. This removed the dye from the nylons.
16. One nylon was placed inside the second to form a double wall and both were stretched directly over a Soxlet extractor chamber.
17. The slurry of methanol/resin was poured (approx. 2 l) was full of resin to just below the side arm, and the nylon tied off.
18. The resin was extracted twice for 24 hours (each time replacing the solvent) with methanol and ethyl acetate (Resi-grade) for a total of 4 days.
19. The cylinder of nylon/resin was removed and the resin poured into a 21 cm x 21 cm rectangular pyrex dish.
20. The resin was dried in a vacuum oven (25") for 3-4 days at 65°C.
21. The resin was transferred to a clean glass bottle for storage.

Note: XAD-4 resin, Rohm-Hass & distributed by Supelco.

(7) Gas Chromatography

Analysis of the second set of validation samples, submitted air samples and quality assurance samples was accomplished with a Varian Model 6500 gas chromatograph equipped with a thermionic specific detector (N/P) and a Varian Vista Model 402 data system. The column was a "Megabore" 30 m x 0.53 mm ID DB-5. Flows for helium carrier, makeup, air and hydrogen were 12, 20, 175, 4.5 ml/min, respectively. Oven temperature program was 160°C initial with 2 minute hold, and programmed to 250°C at 10°C/minute with a final hold of one minute. This resulted in a total run time of 12 minutes. The retention time of carbofuran was 6.27 minutes.

(8) Method Validation

On 4/9/93, three unused prepared samples (30 mL of XAD-4 in a screw-top glass jar) were each fortified by adding 1.00 µg of carbofuran (1.00 ml of 1.00 ng/µl in ethyl acetate) slowly on top of the resin using a volumetric pipette. The solvent was allowed to evaporate, and 75 ml of ethyl acetate was added to each jar. The jars were capped and then placed on a rotating platform for a minimum of 30 minutes. The 35 ml of each extract was evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results are shown in Table IV and had good extraction recoveries (>90%) from the resin.

Table IV, Method validation Samples

Sample	µg Spiked	Total µg	% Recovery
AR I	1.00 µg	0.98 µg	98%
AR II	1.00 µg	0.97 µg	97%
AR III	1.00 µg	0.90 µg	90%
			average = 95% ± 3 SEM

(9) Submitted Air Samples

On 4/5/93, Jack Rogers delivered a total of 37 samples in an ice chest with "Blue Ice" bags. The samples were inspected, placed into a -20°C freezer and assigned unique TAL log numbers. The ARB log numbers for these samples were 6 to 42. On 4/9/93 (4 days from receipt) all samples were removed from the freezer and allowed to come to room temperature. Seventy-five ml of ethyl acetate was added to each jar. The jars were capped and then placed on a rotating platform for a minimum of 30 minutes. The 35 ml of each extract was evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results are shown in Table V. The limit of quantitation (LOQ) for carbofuran was established at <0.3 µg total per sample. The LOQ was defined at being five times the baseline noise. A calculation is:

<0.3 µg = (<0.20 ng/3 µl injected) x (2 ml final volume) x (75 ml orig vol/35 ml taken)

Table V, Submitted Air Samples

ARB Log #	ARB ID	Total µg
6	ON-1	<0.3
7	ON-2	<0.3
8	OE	<0.3
9	OS	<0.3
10	OW	<0.3
11	1N-1	<0.3
12	1N-2	<0.3
13	1E	0.9
14	1S	<0.3
15	1W	0.3
16	2W	1.3
17	2N-1	0.9
18	2N-2	0.6
19	2E	0.4
20	2S	<0.3
21	2B	<0.3
22	3W	1.8
23	3N-1	1.9
24	3N-2	2.3
25	3E	0.9
26	3S	<0.3
27	4W	0.9
28	4N-1	0.7
29	4N-2	0.7
30	4E	0.5
31	4S	<0.3
32	5W	0.3
33	5N-1	0.7
34	5N-2	0.8
35	5E	2.0
36	5S	1.1
37	6W	0.8
38	6N-1	1.3
39	6N-2	1.3
40	6E	2.6
41	6S	1.0
42	6B	<0.3

(10) Submitted Quality Assurance Samples

On 4/15/93, seven quality assurance samples were delivered by courier. These samples were immediately assigned TAL log numbers and analyzed. Seventy-five ml of ethyl acetate was added to each jar, and the samples were analyzed as in Section 4. The carbofuran results are shown in Table VI.

Table VI, Submitted Quality Assurance Samples

ARB Log #	ARB ID	Total µg
n/a	CBF-1	4.8
n/a	CBF-2	3.2
n/a	CBF-3	9.4
n/a	CBF-4	2.8
n/a	CBF-5	<0.3
n/a	CBF-6	4.5
n/a	CBF-7	9.7

APPENDIX V

QMOSB AUDIT REPORT

June 30, 1993

AUDIT REPORT

CARBOFURAN MONITORING IN IMPERIAL COUNTY

SUMMARY

Between March 31 and April 2, 1993, the Engineering Evaluation Branch of the California Air Resources Board conducted ambient air sampling to document the airborne emissions of Carbofuran during an application in Imperial County, California. The samples were analyzed by the Trace Analytical Laboratory of the UC Davis Department of Environmental Toxicology.

On March 11, staff of the Quality Assurance Section of the Air Resources Board conducted flow rate audits of the air samplers used in the monitoring of Carbofuran. The audits were conducted with a mass flow meter traceable to the National Institute of Standards and Technology. The difference between the reported and true flow rates averaged -0.6% with a range of -1.2% to 0%.

A system audit of the Trace Analytical Laboratory was conducted to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that these were consistent with good practice. The only deficiencies noticed were the lack of control charts or response factor plots, and field spikes.

On April 15, seven samples spiked with measured amounts of Carbofuran were submitted to the laboratory for analysis. The samples were prepared from a 0.2 mg/ml Carbofuran solution obtained from Chem Service. The difference between the assigned and the reported Carbofuran mass averaged -4.0% and ranged from -10.0% to 5.0%.

AUDIT REPORT

CARBOFURAN MONITORING IN IMPERIAL COUNTY

INTRODUCTION

Between March 31 and April 2, 1993, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted ambient air sampling to document the airborne emissions of Carbofuran during an application in Imperial County, California. Samples were collected in the vicinity of the treated field by drawing ambient air at measured rates through sampling cups containing an adsorbant resin. The samples were later analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology. Gabriel Ruiz of the CARB's Quality Assurance (QA) Section conducted a flow rate audit of the air samplers, a system audit of the field and laboratory operations, and a performance audit of the analytical method.

FLOW RATE AUDIT

On March 11, 1993, a flow rate audit of the five air samplers used by the EEB in the monitoring of Carbofuran was conducted at the EEB's shop in Sacramento, before the samplers were deployed in the field.

Each sampler consisted of a sampling cup connected with Teflon tubing to an in-line control valve, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of electrical conduit.

The samplers' flow rates were set by connecting a calibrated rotameter to the inlet of the sampler and adjusting the control valve on the sampler so that the flow rate indicated by the rotameter was about 12.4 liters per minute (lpm). The actual flow was then calculated from the rotameter's calibration and reported as the sample collection flow rate.

The flow rate of each sampler was audited with a 30 lpm Matheson mass flow meter traceable to the National Institute of Standards and Technology, following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged -0.6% and ranged from 0% to -1.2% (Table 1).

During the actual sampling period, the flow rate of some samplers dropped considerably, thus making necessary an audit of the rotameter over the full range of flow rates observed. The rotameter was audited on April 6, 1993, and the difference between the reported and the true flow rates averaged -0.8%, and ranged from 0% at 16.2 lpm to -2.0% at 9.6 lpm (Table 2).

Table 1. Results of the flow rate audit of the air samplers used in the monitoring of Carbofuran.

Sampler	Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
1	12.3	16.0	16.0	0
2	12.6	16.4	16.6	-1.2
3	12.5	16.3	16.5	-1.2
4	12.4	16.1	16.1	0
5	12.4	16.1	16.2	-0.6

Table 2. Results of the flow rate audit of the rotameter.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
12.4	16.2	16.2	0
12.0	15.6	15.6	0
11.5	14.8	15.0	-1.3
8.0	9.6	9.8	-2.0

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

SYSTEM AUDIT

A system audit of the field and laboratory operations was conducted to evaluate the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation. The audit was conducted by reviewing the method validation data sent to the CARB and through a telephone conversation with Chuck Mourer of the TAL. The following is a discussion of the audit findings.

Sample Handling and Storage

Sampling was conducted by staff of the ARB's EEB, following the schedule specified in the sampling protocol. After sampling, the exposed XAD-4 resin was collected into clean 4-oz glass jars with teflon-lined lids. The samples were stored over dry ice in an ice chest until they were delivered to the laboratory at the end of the sampling period.

Upon receipt at the laboratory, the samples were logged in and stored in a freezer at -20°C. Extraction and analysis of the samples were carried out within three days of receipt.

Sample Analysis

The analytical method was developed by laboratory staff and is described in a document entitled "Pilot Monitoring Study of Two Pesticides in Air." The method entails extraction of the XAD-4 resin with ethyl acetate, evaporation to dryness, addition of 2 ml ethyl acetate, and analysis by gas chromatography (refer to the protocol available in the QA office for further details). Analyses were performed with a Varian Model 6500 gas chromatograph equipped with a thermionic specific nitrogen-phosphorus detector and a Varian Vista Model 402 data system.

The analyses were conducted in duplicate. The calibration standards were prepared within ten days of the date of analysis and had concentrations of 0.12, 0.25, 0.50, and 1.0 ug/ml. The total Carbofuran mass was calculated from the height of the peaks on the chromatogram.

Quality control activities performed to monitor and document the quality of the data included analysis of three laboratory spikes, one method blank, one field blank, and seven duplicate samples. The response factor of the calibration standards was monitored by the analyst to confirm the instrument's stability, but the results were not plotted on a control chart. The study did not include field spikes.

Method Validation

The limit of detection (LOD) was determined as the total mass equivalent to the concentration of the second-lowest calibration standard. The LOD was calculated as 0.375 ng per sample. The laboratory set the limit of quantitation as 0.5 ug per sample.

A trapping efficiency study was conducted by drawing ambient air at 48 to 67 lpm for 24 hours through triplicate assemblies, each consisting of a funnel spiked with 100 ug of Carbofuran, and two sampling cups (primary and secondary) connected in series. At the end of the run, each component was extracted and analyzed separately. The trapping efficiency averaged 90.6%, and no Carbofuran was detected in the secondary sampling cups.

The method recovery rate was determined by spiking resin samples in triplicate with 1.0 ug of Carbofuran. The recovery rates averaged 95%. In a previous study, three pairs of resin samples were spiked with 1, 10 and 100 ug of Carbofuran, and the recoveries averaged 99.2%, 98.7%, and 107.9%, respectively.

Stability studies were conducted by spiking resin samples in triplicate with 1, 10, and 100 ug of Carbofuran and storing them at -20°C for twelve days. The recoveries averaged 107.0%, 110.1%, and 91.7%, respectively.

Documentation

All the samples received at the laboratory were accompanied by ARB's chain-of-custody records. Upon receipt, the samples were inspected and logged into an electronic file . The field sample number of each sample was recorded, and a unique laboratory number was assigned.

Field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date of analysis, results, and analyst. The raw analytical data and the results of the analyses were stored in an electronic spreadsheet. Hard copies of the run data and the chromatograms were saved in an accessible form.

LABORATORY PERFORMANCE AUDIT

The accuracy of the TAL's analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of Carbofuran. The samples were prepared on April 15, 1993, following the procedures outlined in Attachment II. The samples were delivered to the laboratory on the same day, and they were extracted and analyzed immediately.

The difference between the assigned and the reported Carbofuran mass averaged -4.0% and ranged from -10.0% to 5.0% (Table 3), which is consistent with the reported method recoveries. The results of duplicate samples indicate a high degree of precision for the method.

Table 3. Results of TAL's analyses of Carbofuran audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
CBF-1	5.0	4.80	-4.0
CBF-2	3.0	3.15	5.0
CBF-3	10.0	9.37	-6.3
CBF-4	3.0	2.84	-5.3
CBF-5	0	<0.5	N/A
CBF-6	5.0	4.50	-10.0
CBF-7	10.0	9.67	-3.3

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures, the analytical methodology, and the method validation were appropriate; and the results of the analytical performance audit were in excellent agreement with the expected values.

The only deficiencies noticed were the lack of control charts or response factor plots, and the omission of field spikes. A control chart would demonstrate statistical control of the method and document its uncertainty. Response factor plots would allow the analyst to monitor the instrument's sensitivity over time, so that changes such as degradation of the column, the detector, or the standards could be detected. Finally, field spikes should be included with each batch of samples submitted to the laboratory to monitor sample recovery.

Flow Audit Procedure for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is placed in series with the sampler's inlet and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the outlet port of the sampler's flow control valve to the inlet port of the audit device with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

Performance Audit Procedure
For The Laboratory Analysis Of Carbofuran

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Carbofuran. The audit is conducted by submitting audit samples spiked with known concentrations of Carbofuran. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Carbofuran, 0.2 mg/ml in Ethyl Acetate, Chem Service #F2006.
2. Ethyl Acetate, nanograde.
3. XAD-4 Resin.
4. Glass Jars, 4 FL OZ, 58-mm diameter.
5. 50 ul Microsyringe.

Safety Precautions

Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Sample Preparation

Prepare seven audit samples from the 0.2 mg/ml Carbofuran spiking solution according to the following table:

Sample	0.2 mg/ml Carbofuran Volume (ul)
CBF-1	25
CBF-2	15
CBF-3	50
CBF-4	15
CBF-5	0
CBF-6	25
CBF-7	50

1. Measure 30 ml of XAD-4 resin into a glass jar.

2. Transfer the appropriate volume of the Carbofuran spiking solution onto the resin with the syringe, using a circular motion while slowly pushing the plunger. Do not allow the solution to run down the sides of the jar. Touch off any remaining droplets of the solution onto the resin, and shake off any resin adhering to the needle by tapping it gently against the rim of the jar.

3. Cover the jar with the plastic cap provided.

4. Label each jar with its assigned number and store in a freezer until ready for analysis.